Further Studies on Phenolic Hexa-
methylenetetramine Compounds

DISSERTATION

BY

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### TETRAMINE COMPOUNDS

The production of resins or resinoid substances of the Bakelite type[1] by the interaction of phenols with compounds containing an active methylene group has, of late, acquired considerable importance in the industry of coal-tar derivatives. The increasing number of applications of these products in the most diversified fields is stimulating research in many directions. That this industry was born and developed in the United States, which to-day is still the leader in this branch of chemical industry, adds interest to any subject of research which directly or indirectly may throw light on the unusually complicated chemistry of this subject.

The theoretical interpretation of the different phases of the Bakelite reaction is not by any means an easy one, and considerable additional research work will be required before permitting ourselves to do much beyond guessing at what really happens. In the meantime, the careful study of the formation of intermediate products can render us considerable help in this subject. Among these intermediate products, the further advances are amorphous mixtures which are not amenable to the usual methods of chemical purification or isolation. Therefore, it is more natural to start first with the intermediates which are well-defined crystalline bodies of which the chemical composition can be determined by well-established methods. The present research work was, therefore, confined to some of the first phases of the reaction, and more particularly to such bodies as are liable to form when ammonia is used in the process, either as such or in the shape of hexamethylene-tetramine.

In the formation of these products of the Bakelite type the methylene-containing body may be com-

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[1] These substances are also known under other trade names, as for instance, Condensite, Resinit, Sipilite, Redmanol, etc.

mercial formaldehyde solution—known as formalin, formol, etc. This commercial product is practically a mixture of several bodies containing active methylene groups, as, for instance, methylal, formaldehyde, the polymers of formaldehyde, their hydrates, etc. The reaction is favored by the addition of so-called condensing agents, or catalysts—whatever that may mean. Acids, salts, and alkalies have been used for this purpose. In some cases where particular effects have to be obtained, ammonia is preferable. If ammonia is added to formaldehyde or to mixtures of phenol and formaldehyde, the ammonia disappears immediately and becomes hexamethylenetetramine:

$$
\begin{array}{c}
N \\
CH_2 \quad CH_2 \quad CH_2 \\
N \\
CH_2 \quad CH_2 \\
N \quad\quad N \\
CH_2
\end{array}
$$
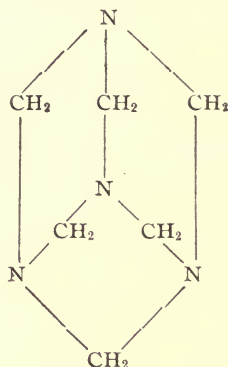
so that all these reactions wherein formaldehyde and ammonia are used conjointly can be repeated by the direct use of hexamethylenetetramine. But in presence of phenol, the hexamethylenetetramine does not remain as such. It combines with the phenol in the proportion of three molecules of phenol to one molecule of hexamethylenetetramine and produces a well-defined crystalline product, hexamethylenetetramine triphenol, which has been described by Moschatos and Tollens.[1]

In 1909, Lebach[2] pointed out that whenever ammonia is used in the Bakelite reaction, hexamethylenetetramine triphenol is formed in the first stages of the process. Under the action of heat, this product undergoes a further decomposition and resinifies, emitting ammonia.[3]

Contrary to the results of Moschatos and Tollens, who were unable to prepare addition products of

[1] *Ann.*, **272** (1892), 271.
[2] *Z. angew. Chem.*, **22** (1909), 1600; *J. Soc. Chem. Ind.*, **32** (1913), 559.
[3] A resumé of the literature on this subject is given by L. H. Baekeland, in "The Chemical Constitution of Resinous Phenolic Condensation Products," *J. Ind. Eng. Chem.*, **5** (1913), 506.

hexamethylenetetramine with any of the three cresols or with carvacrol or thymol, Baekeland had succeeded in his laboratory in preparing a corresponding crystalline cresol derivative, but inasmuch as this work had not been carried out with each one of the completely purified cresols and studied by itself, it seemed desirable that each one of the three homologs should be studied separately as to its individual behavior. This research was also extended to carvacrol and the results obtained thus far are set forth. Similar compounds obtained from other phenolic bodies are now under study. In the meantime, the observations concerning the new cresol derivatives are submitted in the present paper.

The reason of the non-success of Moschatos and Tollens in making the cresol derivatives of hexamethylenetetramine is, mainly, that the isolation of these substances is incomparably more difficult than in the case of phenol. The hexamethylenetetramine triphenol forms rapidly and visibly under almost all circumstances, and crystallizes very well from aqueous solutions or even from solutions when a considerable excess of one of the constituents is used. This is not the case with some of the cresol derivatives. The temperature at which they form lies in some cases so close to the temperature at which they decompose that their formation is almost sure to be overlooked if proper precautions are not taken. Furthermore, some of those products have a tendency to remain liquid in the presence of an excess of some of the reacting products or impurities. That such products exist has been established beyond doubt by the present investigation.

In this work data were determined for the relationship of certain of the phenolic condensation products. The results are appended.

HEXAMETHYLENETETRAMINE TRIPHENOL

Moschatos and Tollens made the easily prepared hexamethylenetetramine triphenol by mixing 6 g. of a concentrated water solution of hexamethylenetetramine with a concentrated solution containing 6 g. of phenol. The product isolated had the following composition:

	Calculated for $C_6H_{12}N_4.3C_6H_5OH$ Per cent	Found by M. and T.			
		1	2	3	4
			Per cent		
C_{24}	68.25	68.49	68.09	...	...
H_{30}	7.11	7.34	7.44	...	...
N_4	13.27	...	...	13.65	13.77

All the phenols do not react with hexamethylene-tetramine to form an addition product in which there are one mole of hexamethylenetetramine and three moles of the phenol. The various groupings about the benzene ring seem to determine the extent to which the addition takes place. The three cresols whose structural formulas are nearly identical with that of ordinary phenol and whose properties are somewhat similar to the latter should form addition compounds the same as does phenol.

HEXAMETHYLENETETRAMINE DI-*m*-CRESOL

The *m*-cresol addition product is the most easily obtainable. At first ordinary *m*-cresol was used in both dilute and concentrated alcoholic solutions; but the expected crystalline intermediate addition products did not appear. The alcoholic solutions were refluxed several hours and the concentrated solutions allowed to stand several weeks to see if the compound would crystallize out. No crystalline product was obtained in this case. There must have been some impurity in the cresol that hindered the formation, for with cresol purified according to Fox and Barker[1] the product crystallized out in 40 min.

A mixture of 315 g. of *m*-cresol and 136 g. of hexa-methylenetetramine was heated for an hour in 80 cc. of a 60 per cent (60 parts by volume of alcohol and 40 parts by volume of water) alcoholic solution. Too much heating caused the addition product to decompose and pass over into the noncrystallizing resinous material. By withdrawing portions of the mixture from time to time, and cooling slightly, it could be observed, by the formation of crystals, when the most favorable point was reached before resinification set in. On stopping the heating, crystals appeared even in the hot solution. The crystals were filtered off and pressed on a porous tile to get rid of the adhering sirupy material. The product was then dissolved in hot 95 per cent alcohol. On cooling, long, fine, needle-like crystals separated out.

Analysis showed that the substance was not formed on a 1:3 basis as is the case with the ordinary hexa-methylenetetramine triphenol, but was an addition product of 1 mole of hexamethylenetetramine and 2 moles of *m*-cresol.

[1] *J. Soc. Chem. Ind.*, **37** (1918), 260.

Calculated for $C_6H_{12}N_4.2C_6H_4OH.CH_3$	1	2	Found 3	4	Av.
Per cent			Per cent		
C_{20}.......... 67.40	67.45	67.23	...	...	67.34
H_{29}.......... 7.87	8.03	7.80	...	...	7.96
N_4.......... 15.73	...	...	15.59	15.80	15.69

Hexamethylenetetramine di-*m*-cresol has not a true melting point, since when the substance is held at a temperature around its point of liquefaction, 90° C., it undergoes decomposition, passing over into the irreversible resinous stage. The compound is very soluble in hot 95 per cent alcohol, the solubility increasing with the temperature. A characteristic feature is that when it is placed in a sufficient amount of water or ether there is a very decided tendency towards a splitting of the product. In water the solubility of the hexamethylenetetramine shows up predominantly, as it is dissolved by the water leaving insoluble cresol as an oil. In ether the solubility of the *m*-cresol predominates, and the compound breaks up leaving the insoluble hexamethylenetetramine as a precipitate. The solubility in benzene is moderate, but increases with the temperature. Acetone has the same effect on the substance as has ether, that is, breaking up the structure by dissolving out the soluble cresol and leaving the insoluble hexamethylenetetramine.

HEXAMETHYLENETETRAMINE DI-*p*-CRESOL

Pure *p*-cresol was first made from *p*-toluidine. When it was found that an addition product was formed with hexamethylenetetramine, a larger quantity of the material was made by the method given by Fox and Barker.[1]

A mixture of 385 g. of *p*-cresol and 167 g. of hexamethylenetetramine in 150 cc. of 95 per cent alcohol was heated on a steam bath for 1.5 hrs. The same precaution must be observed here as in the case of the formation of the *m*-cresol compound. On allowing the liquid to stand at room temperature, crystals separate out. The compound was recrystallized from 50 per cent alcohol.

The addition product has no melting point, but begins to resinify at the temperature of liquefaction, 87.0° C. The decomposition is shown when the substance turns brown and partially resinifies upon heating in a sealed glass tube for 3 hrs. at a temperature of 90° to 100°.

Analysis shows that it has the same proportion of the two constituents as the *m*-compound, namely,

[1] *Loc. cit.*, p. 268.

1 mole of hexamethylenetetramine and 2 moles of p-cresol.

	Calculated for $C_6H_{12}N_4.2C_6H_4OH.CH_3$ Per cent		Found			
		1	2	3 Per cent	4	Av.
C_{20}	67.40	67.18	67.35	...	...	67.27
H_{28}	7.87	8.20	8.01	...	...	8.10
N_4	15.73	...	...	15.82	15.71	15.76

The same qualitative solubilities as applied to the m-cresol product apply to the p-cresol compound.

HEXAMETHYLENETETRAMINE MONO-o-CRESOL

Pure o-cresol was made according to the method of Fox and Barker.[1]

A mixture of 475 g. of o-cresol and 205 g. of hexamethylenetetramine in 100 cc. of 95 per cent alcohol was heated on a water bath for 2.5 hrs. On allowing to cool at room temperature, crystals separated out. These were recrystallized from 95 per cent alcohol.

The compound behaves somewhat differently from the p- and m-cresol addition products, since on heating there was no sharp melting point to the liquid stage, followed by a final passing over to the resinous material. A small portion seemed to soften on heating and show signs of melting, but most of the substance either sublimed or charred.

Analysis showed that the proportion of hexamethylenetetramine to o-cresol was 1 : 1.

	Calculated for $C_6H_{12}N_4.C_6H_4OH.CH_3$ Per cent		Found		
		1	2 Per cent	3	4
C_{13}	62.90	63.12	63.20	...	...
H_{20}	8.07	8.07	7.94	...	...
N_4	22.55	...	...	22.74	22.69

It was thought that it might be possible to isolate a compound of o-cresol which would have the same proportions of the two constituents as have the p- and the m-cresol intermediates. The crystals of hexamethylenetetramine were dissolved directly in the o-cresol, and with portions of this solution various runs were made in which the time factor of heating was the variable. Heating was accomplished on a water bath, the time varying from 2 to 10 hrs. For the runs with a small amount of heating the solution was clear, while with the runs extending over 10 hrs. the solution was dark brown, showing that a reaction had set in with the formation of the resinous material. After allowing the solutions to stand several days the crystals were filtered off, pressed on porous tile, and recrystallized from alcohol. In all cases analysis

[1] *Loc. cit.*

of the crystals showed that the product was a compound with a 1 : 1 proportion of hexamethylenetetramine and *o*-cresol.

Crystals obtained after 8 hrs.' heating showed the following composition:

	Calculated for $C_6H_{12}N_4.C_6H_4OH.CH_3$ Per cent	Found Per cent
C_{12}	62.90	63.04
H_{20}	8.07	8.22
N_4	22 55	22.70

From this it appears that there is but one addition product of *o*-cresol and hexamethylenetetramine, and that is with one mole of each of the two constituents present.

HEXAMETHYLENETETRAMINE HYDROQUINOL

Moschatos and Tollens[1] give for the preparation of this compound 4 g. of hexamethylenetetramine in 5 g. of water mixed with 33 g. of hydroquinol in 4 g. of water. The product, purified by washing with water and with ether, and drying over sulfuric acid, analyzed as follows:

	Calculated for $C_6H_{12}N_4.C_6H_4(OH)_2$ Per cent	Found by M. and T. 1	2	3
C_{12}	57.60	57.20	...	...
H_{18}	7.20	7.77	...	...
N_4	22.40	...	22.57	22.47

This was checked up as follows: 5 g. $C_6H_4(OH)_2$ in 9 cc. of water were mixed with a solution of 6 g. of hexamethylenetetramine in 10 cc. of water. The solution was heated on a water bath for 30 min., then allowed to stand over night. Crystals washed with water, then ether, and dried over sulfuric acid. Analysis showed:

	Calculated for $C_6H_{12}N_4.C_6H_4(OH)_2$ Per cent	Found Per cent
C_{12}	57.60	57.35
H_{18}	7.20	7.11
N_4	22.40	22.46

On heating, part of the compound sublimed and part charred with very little melting. This behavior is similar to that of the hexamethylenetetramine *o*-cresol compound.

HEXAMETHYLENETETRAMINE RESORCINOL

Moschatos and Tollens formed the compound by heating a mixture of 2 g. of hexamethylenetetramine dissolved in 3 g. of water and 3 g. of resorcinol dissolved in 3 g. of water. The composition of the compound was found by Moschatos and Tollens to be as follows:

[1] *Ann.*, **272** (1892–3), 282

	Calculated for $C_6H_{12}N_4.C_6H_4(OH)_2$	Found by M. and T.			
	Per cent	1	2	3	4
		Per cent			
C_{12}	57.60	37.14	57.35	...	...
H_{18}	7.20	7.43	7.42	...	...
N_4	22.40	...	...	22.09	22.32

By following the same order of procedure as outlined above, a precipitate was easily obtained. On analysis the composition was found to be the same as that represented by Moschatos and Tollens:

	Calculated Per cent	Found Per cent
C_{12}	57.60	57.39
H_{18}	7.20	7.10
N_4	22.40	22.34

This compound also shows no melting point, which is similar to the hydroquinol and the *o*-cresol intermediates. It seems to be a characteristic feature of the hitherto observed phenol hexamethylenetetramine compounds that it is necessary that there be at least 2 moles of the phenol to 1 of the hexamethylenetetramine in order that there be a well-defined point of liquefaction.

HEXAMETHYLENETETRAMINE CARVACROL

The carvacrol obtained for use in this work was made from cymene.[1] It ran 93 per cent pure, the other constituents being approximately 6 per cent thymol and 1 per cent thiophenols. The product was purified according to the method developed by Mr. Allan Leerburger:

A very stiff paste of the carvacrol and lead acetate was allowed to stand at room temperature for 30 hrs. The mass was broken up and the phenols extracted with petroleum ether. The carvacrol-lead acetate compound is soluble in the petroleum ether, whereas the thymol-lead acetate is insoluble in the ether, giving a means of separating the two phenols. After allowing the petroleum ether to evaporate, the liquid was washed with a normal solution of mercuric chloride (using as the solvent 50 parts by volume of water and 50 parts by volume of alcohol). This removes the thiophenols, leaving the carvacrol as the oil. The carvacrol then distilled in a 4-bulb fractionating column, the portion boiling between 237° and 239° C. being taken.

One mole of hexamethylenetetramine in just sufficient 95 per cent alcohol to dissolve the crystals was mixed with 3 moles of the purified carvacrol. The mixture was heated on a water bath for 40 hrs., then allowed to stand at room temperature for 1 wk. The uncrystallized mass was dissolved out by mixing with kerosene. The fine precipitate was filtered, and the crystals dissolved in hot 95 per cent alcohol.

[1] Hixson and McKee, *J. Ind. Eng. Chem.*, **10** (1918), 982

On cooling the alcoholic solution the compound crystallized out readily. Further purification was made by repeating the crystallization from hot 95 per cent alcohol.

The compound shows a point of liquefaction at 148° C., at which point it resinifies quickly. It is very soluble in hot 95 per cent alcohol, but insoluble in the cold alcohol. An important point is that it is very soluble in ether and acetone. Some of the cresol compounds, as has been stated, may be broken up in water, ether, and acetone, the two latter solvents dissolving out the easily soluble cresols and leaving the insoluble hexamethylenetetramine as a precipitate. This difference in solubility between the carvacrol and cresol compounds may be due to the difference in linkings of different phenols with the hexamethylenetetramine.

Analysis showed that the compound was not of the same order of addition as were cresol and phenol products, which were in the proportion of 1 mole of hexamethylenetetramine to 2 moles of the *m*- or *p*-cresol, and 3 moles of phenol to 1 mole of hexamethylenetetramine. The composition was found to be as follows:
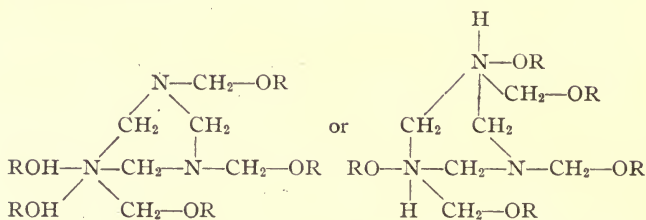
	Run 1 Per cent	Run 2 Per cent	Average Per cent
Carbon	76.95	77.10	77.02
Hydrogen	9.20	9.27	9.23
Nitrogen	4.92	4.99	4.96

From the table below it is clearly seen that the hexamethylenetetramine is not directly added to the carvacrol as it is in the case of the cresols and phenols.

	$C_6H_{12}N_4.C_{10}H_{14}O$	$C_6H_{12}N_4.2C_{10}H_{14}O$	$C_6H_{12}N_4.3C_{10}H_{14}O$	Found
Carbon	66.25	71.00	73.25	77.02
Nitrogen	19.35	12.75	9.50	4.96
Hydrogen	8.96	9.10	9.16	9.23

The percentages found do not correspond to any simple proportion of addition, as was shown in the case of the other phenols mentioned. However, if we assume that a nitrogen is broken out of the structure of the hexamethylenetetramine to form ammonia with hydrogens of the hydroxyls of 3 moles of carvacrol, and further that 2 moles are taken up additively by one or two of the other nitrogens, the percentages of carbon, hydrogen, and nitrogen correspond exactly with the percentages as found. The smell of ammonia toward the end of the heating in the formation of this compound seems to bear out this point that ammonia is split out, but no quantitative determination has thus far been undertaken. The diagrams, in which R represents the radical

part of the carvacrol structure, illustrate possible arrangements.

$$
\begin{array}{cc}
\text{N—CH}_2\text{—OR} &
\begin{array}{c}
\text{H} \\
| \\
\text{N—OR} \\
\diagup \ |\ \diagdown\text{CH}_2\text{—OR}
\end{array}
\end{array}
$$

It is to be pointed out that although the interpretation of the structure of hexamethylenetetramine is thus far rather arbitrary, and although the correct one may be found to be quite different from the above, the percentages of elements will in all cases be the same for the theoretical carvacrol compound.

	Calculated from Above Structure Per cent	Found Per cent	Deviation Per cent
Carbon	76.95	77.02	0.07
Nitrogen	4.84	4.96	0.12
Hydrogen	9.10	9.23	0.13

All this becomes rather easy of interpretation if in the formation of the hexamethylenetetramine carvacrol compound there has been 1 mole of ammonia split out and there have been 2 moles of carvacrol added to one of the nitrogen.

ENERGY RELATIONSHIP OF PHENOLIC HEXAMETHYLENE COMPOUNDS

APPARATUS—For the heat of combustion of the phenol, hexamethylenetetramine, and hexamethylenetetramine triphenol, an Emerson adiabatic bomb calorimeter provided with a proper stirrer and a Beckmann thermometer graduated to give an estimated reading of 0.001° were used. For the heat of solution the bomb was eliminated and the metal can for the water replaced by a glass container. The substance whose heat was to be determined was held in a glass-stoppered weighing bottle, the cover of which was removed by small wires passing through the third hole in the top of the calorimeter jacket.

DATA—The water equivalent of the calorimeter was determined in the ordinary way by burning a material whose heat of combustion was known. Naphthalene from the U. S. Bureau of Standards laboratory was used. By weighing the separate parts of the bomb and accessories, the water equivalent of the bomb was found to be 453 g.; without the bomb it was found to be 70 g. The error in the first number was

±2 g., and that in the second number was ±5 g.
Checking these values against other standard sub-
stances, 6320 was obtained for benzoic acid, whereas
the Bureau of Standards gives 6329 cal. per g. as the
correct result. The second value was used in finding
the heat of solution of as pure sodium hydroxide as
could be made without wasting too much time. The
following shows a comparison of the heat of solution
of sodium hydroxide as determined by Thomsen, and
by Berthelot, and as obtained in this study:

		Kg. Cal.
Thomsen	....	9.94
Berthelot	....	9.78
Present work	....	9.85

The errors here would seem to be due to the varied
purity of the NaOH used, rather than to the manipu-
lation of the apparatus.

(*a*) *Heat of solution of hexamethylenetetramine.*

	Kg. Cal.
Run 1	4.902
Run 2	4.896
	———
AVERAGE	4.899[1] (where 1 Cal. = 1000 small calories)

[1] Delepine (*Bull.*, [3] **15**, 1200) gives the heat of solution of hexa-
methylenetetramine at 15° C. as 4.8 Cal.

(*b*) *Heat of solution of phenol.*

	Kg. Cal.
Run 1	—2.92
Run 2	—2.87
	———
AVERAGE	—2.89[1]

[1] Landolt and Bornstein, 3rd Ed., p. 419, give for the heat of solution
of phenol —2.6 Cal.

(*c*) *Heat of reaction of phenol and hexamethylene-
tetramine in an aqueous solution*—In this observation
the phenol was first added to the water, then solid
hexamethylenetetramine added in the manner stated
above. The excess of rise of temperature above that
given by the hexamethylenetetramine would be due
to the reaction of the amine and the phenol. This
is the weak point of this method of determining the
heat of formation of hexamethylenetetramine tri-
phenol, since it is difficult to obtain accurately the
amounts of amine and phenol that have combined
in solution. After the reaction the hexamethylene-
tetramine solution was distilled to obtain the phenol,
the amount of which was determined by the tribromo-
phenol method.[1] The error in this way would be in
the dissociation of the triphenol compound on dis-·

[1] Allen's "Commercial Organic Analysis," 8th Ed., Vol. 3, p. 307.

tillation of the phenol. It was found that the energy reaction was

$(CH_2)_6N_4Aq. + 3C_6H_6OAq. = (CH_2)_6N_4.3C_6H_6O.Aq. + 3.739$ Cal.

(d) *Heat of formation of hexamethylenetetramine.*

Heat of combustion of commercial hexamethylenetetramine:
Run 1—7.380 Cal. per g. at constant volume
Heat of combustion of hexamethylenetetramine resublimed in laboratory:

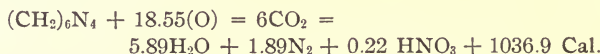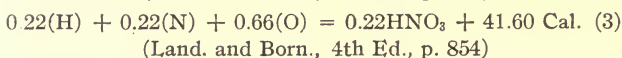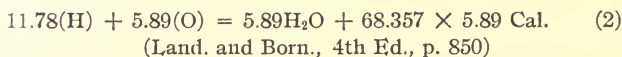|	
Run 2	7.397 Cal. per g. at constant volume
Run 3	7.399
AVERAGE	7.398

By means of the Hempel gas apparatus and freshly prepared solutions of sodium hydroxide and pyrogallol, the following results on the products of combustion were obtained:

PRODUCTS	Actual Result Grams	Theoretical Result Grams
N_2	0.40	0.38
HNO_3	0.119	0.112
CO_2	1.80	1.88

To represent the above results we can write the equation

$(CH_2)_6N_4 + 18.55(O) = 6CO_2 =$
$$5.89H_2O + 1.89N_2 + 0.22\ HNO_3 + 1036.9\ Cal.$$

We know that

$6(C) + 12(O) = 6CO_2 + 6 \times 96.98$ Cal. (1)
(Land. and Born., 4th Ed., p. 855)

$11.78(H) + 5.89(O) = 5.89H_2O + 68.357 \times 5.89$ Cal. (2)
(Land. and Born., 4th Ed., p. 850)

$0.22(H) + 0.22(N) + 0.66(O) = 0.22HNO_3 + 41.60$ Cal. (3)
(Land. and Born., 4th Ed., p. 854)
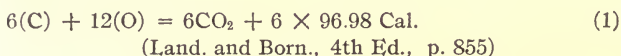
Substituting these three equations in the found equation above, we have:
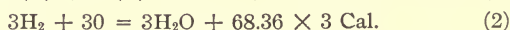
$6(C) + 12(H) + 4(N) = (CH_2)_6N_4 - 43.18$ Cal.
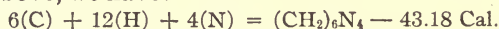
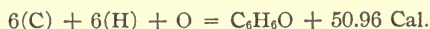Therefore the heat of formation of hexamethylenetetramine $= -43.18$ Cal.

(e) *Heat of formation of phenol*—Berthelot[1] gives the heat of combustion of phenol at constant pressure and 18° C. as 736.00 Cal. per mole.

Required: $6(C) + 6(H) + (O) = C_6H_6O + x$ Cal.

Found: $C_6H_6O + 14(O) = 60\ O_2 + 3H_2O + 736.00$ Cal.

We know that:

$6(C) + 12(O) = 60\ O_2 + 96.98$ Cal. • (1)

$3H_2 + 3O = 3H_2O + 68.36 \times 3$ Cal. (2)
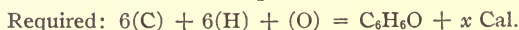
Substituting Equations 1 and 2 in the found equation we obtain

$6(C) + 6(H) + O = C_6H_6O + 50.96$ Cal.

Accordingly the heat of formation of phenol is 50.96

[1] *Ann. chim. phys.*, [6] **3** (1888), 326.

Cal. per mole. This value is different from the one Berthelot gives[1] because he uses the heat of formation of CO_2 as 94.30 Cal. and the heat of formation of water as 69.00 Cal. These values are not considered correct and better values are used in the calculations above.[2] The value 736.00 Cal. per mole for the heat of combustion of phenol is used here because it represents the value obtained in this research.

(f) *Heat of solution of hexamethylenetetramine triphenol.*

Average value obtained was —10.671 kg. Cal.

(g) *Heat of formation of hexamethylenetetramine triphenol.*

The heat of combustion of hexamethylenetetramine triphenol at constant pressure was found to be 3228.30 Cal. per mole.

Required: $24(C) + 30(H) + 3(O) + 4(N) =$
$$(CH_2)_6N_4.3C_6H_6O + x \text{ Cal.}$$

Found: $(CH_2)_6N_4.3C_6H_6O + 30.73(O) =$
$$24CO_2 + 14.71H_2O + 1.71N_2 + 0.58HNO_3 + 3228.30 \text{ Cal.}$$

We know:

$24(C) + 48(O) = 24(CO_2) + 96.98 \times 24 \text{ Cal.}$ (1)

$29.42(H) + 14.71(O) = 14.71H_2O + 68.357 \times 14.71 \text{ Cal.}$ (2)

$0.58(H) + 0.58(N) + 1.74(O) =$
$$58 HNO_3 + 41.60 \times 0.58 \text{ Cal. (3)}$$

Substituting these three equations in the above found equation and solving, we obtain the required equation:

$24(C) + 30(H) + 3(O) + 4(N) =$
$$(CH_2)_6N_4.3C_6H_6O + 128.76 \text{ Cal. per mole}$$

The heat of formation of hexamethylenetetramine triphenol, starting with crystals of phenol and amine, is as follows:

Required: Hexamethylenetetramine + 3 phenol =
$$\text{H.T.P.} + x \text{ Cal.}$$

or $(CH_2)_6N_4(\text{crys.}) + 3C_6H_6O(\text{crys.}) =$
$$(CH_2)_6N_4.3C_6H_6O(\text{crys.}) \times \text{ Cal.}$$

We know:

$6(C) + 12(H) + 4(N) = (CH_2)_6N_4 - 43.18 \text{ Cal.}$ (1)

$18(C) + 18(H) + 3(O) = 3C_6H_6O + 3 \times 50.96 \text{ Cal.}$ (2)

$24(C) + 30(H) + 3(O) + 4(N) =$
$$(CH_2)_6N_4.3C_6H_6O + 128.76 \text{ Cal.} \quad (3)$$

Subtracting (1) and (2) from (3) we obtain:

$(CH_2)_6N_4 3C_6H_6O = (CH_2)_6N_4.3C_6H_6O + 19.06 \text{ Cal.}$

[1] Vol. 2, p. 818.

[2] Landolt and Bornstein, 4th Ed., p. 855.

(*h*) *Heat of combustion of hexamethylenetetramine di-p-cresol.*

AT CONSTANT VOLUME, 20° C.

Cal. per G.

Run 1	8.024
Run 2	7.992

AVERAGE   8.008

(*i*) *Heat of combustion of hexamethylenetetramine di-m-cresol.*

At constant volume and 20° C. = 8.010 Cal. per gram

(*j*) *Heat of combustion of hexamethylenetetramine mono-resorcinol.*

AT CONSTANT VOLUME AND 20° C.

Cal. per G.

Run 1	6.730
Run 2	6.700

AVERAGE   6.715

In the addition reactions of hexamethylenetetramine with a phenol thus far investigated there does not seem to be any definite rule by which one is enabled to determine the number of moles of phenol that will combine with the hexamethylenetetramine.

Falk and Nelson[1] have assumed that in catalytic reactions there are binary and ternary compounds formed. Kendall[2] has called attention to the important general rule that stable addition compounds are formed when there is a marked chemical contrast (acidic and basic) between the two reacting components. Thus in the additive compound formed between organic acids and phenols, the stability is very much greater when the organic acid is strong and the phenol weak, or *vice versa*, than in the case in which both substances exhibit the same degree of acidity. A similar generalization holds for the addition compounds between two acids, or between an acid and a ketone, or an acid and an aldehyde.

In the case of the addition compounds formed in this work we have the phenol acting as the acid and the hexamethylenetetramine as the base. It might be assumed from this and from Kendall's generalization that the greater the chemical conratst the greater the stability of the compounds formed, and the greater the number of moles of phenol combining with the basic hexamethylenetetramine. This is not the case, however, in this instance. The degree of acidity seems to have very little to do with the extent of the

[1] *J. Am. Chem. Soc.*, **37** (1915), 1723.

[2] *Ibid.*, **36** (1914), 2498.

reaction. Ordinary phenol, which is a weaker acid than o-cresol, combines in the proportion of three moles of phenol to one of hexamethylenetetramine, whereas the cresol combines in the proportion of 1:1. Nitric acid, a very strong acid in comparison with the phenol. combines only in the proportion of 1 mole of hexamethylenetetramine to 2 moles of acid. Hence we cannot apply the generalization stated above to the case of phenol addition products. Again, the three cresols have practically the same order of hydrogen-ion concentration,[1] but with the p- and m-compounds there are 2 moles adding, whereas with the o-cresol there is only 1 mole adding to the hexamethylenetetramine.

Since the activity of phenol is greatly diminished in the case of the cresols, by the presence of a methyl group, it might be said that the more negative the benzene ring is made with negative groups (nitro and hydroxy) the greater the activity and the greater the number of moles uniting. With hydroquinol and resorcinol, where there are two hydroxy groups, the opposite is true. They react slowly with hexamethylenetetramine, and then only in the proportion of one mole of the phenol to one of the amine. Picric acid, which contains three nitro groups and one hydroxy group, should represent a substance in which the benzene ring has practically the maximum of negative groups, and hence should have high combining properties. Moschatos and Tollens found that the proportion was only 1:1. As yet no rule can be laid down connecting the acidity, or the degree to which the benzene ring is made negative by negative groupings, with the additive properties of phenols and hexamethylenetetramine.

Why should two moles of p- and m-cresol unite with one mole of hexamethylenetetramine, while only one mole of o-cresol unites with one mole of amine? One difference lies in the structure assumed for the three cresols. The hydroxy group of the p- and m-cresols has on each side of it a hydrogen, while the hydroxy group of o-cresol has a hydrogen on but one side. From this it would seem that the extent of addition depends upon the number and activity of the hydrogens adjacent to the reacting hydroxy group.

The structure of hexamethylenetetramine as given by does not seem to represent all the facts as presented

[1] Scudder, "Conductivity and Ionization Constants."
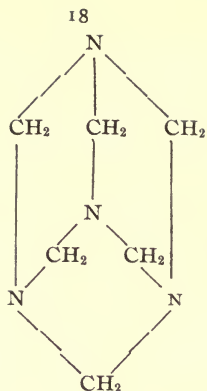
by the addition products with phenols. Here the four nitrogens are all tertiary in character and we should expect that hexamethylenetetramine would add four moles of an alkyl halide. A. Wohl[1] found that but one mole of methyl iodide was taken up additively. In all the phenol addition compounds that have been isolated there is not one case where the number of moles of phenol combining with one mole of hexamethylenetetramine is greater than three. In the carvacrol compound found in this investigation there is strong evidence that one nitrogen is more reactive than the others. This is shown by the fact that ammonia has been split out with one of the nitrogens before one of the other three has added any phenol.

Hexamethylenetetramine is formed from ammonia and formaldehyde. Tertiary amines are formed from ammonia and an alcohol. Alcohol is a lower oxidation product than is the aldehyde. Again, amides are formed from ammonia and an acid, the latter being of a higher oxidation than the aldehyde. From this we might expect that hexamethylenetetramine should not be represented wholly as a tertiary amine, but should exhibit a character midway between the tertiary amine and an amide.

It does not seem from these considerations that the structure of hexamethylenetetramine is properly represented when written in the above manner.

This work was undertaken at the suggestion and under the guidance of Professor L. H. Baekeland. I beg to express my thanks to him and to Professors Thomas B. Rreas, J. M. Nelson, and Ralph McKee, for their valuable advice.

[1] Ber., 19 (1886), 1840

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